Symmetry and Group Theory

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Lecture -60

1) Raman Spectroscopy and 2) Atomic Motions

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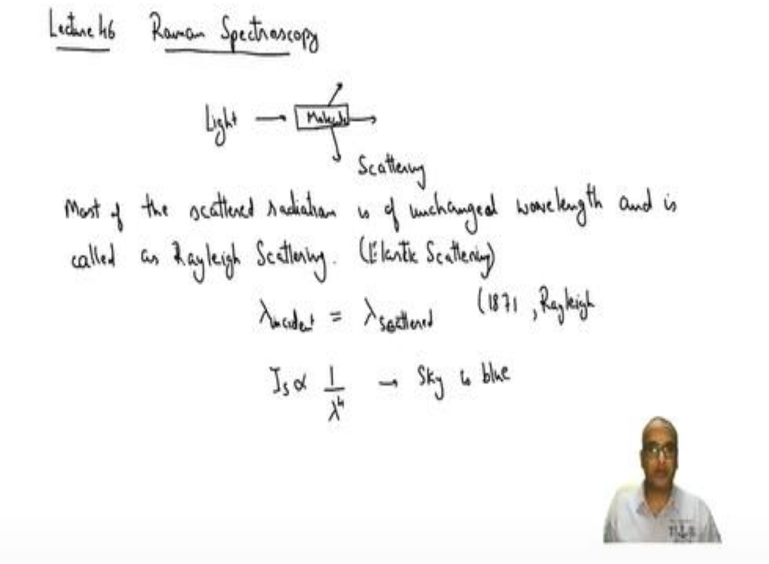

Lecture 46 Raman Spectroscopy

Light → Molecule → Scattering

Most of the scattered radiation is of unchanged wavelength and is called as Rayleigh Scattering. (Elastic Scattering)

$\lambda_{incident} = \lambda_{scattered}$ (1871, Rayleigh

$I_s \propto \frac{1}{\lambda^4}$ → Sky is blue

Welcome back. In today's lecture, we will be discussing Raman spectroscopy. We have already discussed rotational and vibrational. So, we will be discussing Raman spectroscopy and then we will also discuss what are atomic motions, what are different normal modes? So, let us start today's lecture, go to Raman spectroscopy. So, this is highly useful spectroscopy and it is discovered by C V Raman for which he got a Nobel Prize in 1930.

So, let us see so you have light and light is falling onto a molecule, let us say this is my molecule. So, it can have different phenomena of absorption and all but there is one phenomenon which is called as scattering of light. So, this is scattering and most of the scattered radiation, so we will write, most of the scattered radiation is of unchanged wavelength and is called as Rayleigh scattering. So, this is also called as Elastic scattering.

Due to the fact that there is no exchange of energy between light in the molecule. So, incident wavelength is equal to scattered wavelength. This was discovered I think in 1871 by Rayleigh. And the intensity of scattered light is actually proportional to 1 by lambda to the power 4 and this is the reason why sky appears blue. Sky is blue and sun appears red during the morning and evenings.

So, try to find out, try to read more about this Rayleigh scattering. So, we are not going to go into more details, why sky appears blue and all.

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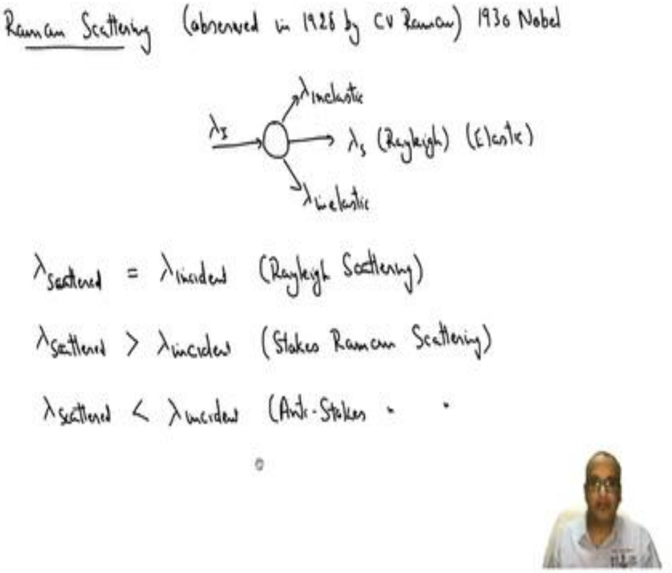

Raman Scattering (observed in 1928 by CV Raman) 1930 Nobel

$\lambda_{scattered} = \lambda_{incident}$ (Rayleigh Scattering)

$\lambda_{scattered} > \lambda_{incident}$ (Stokes Raman Scattering)

$\lambda_{scattered} < \lambda_{incident}$ (Anti-Stokes " "

So, or you must already must have seen this in some course. So, now let us discuss what is Raman scattering? This was observed in 1928 by C V Raman, name which does not need any introduction. And he got 1930 noble for this Nobel Prize. So, what does Raman scattering say? So, if you have a molecule and you have a light which is incident. So, lambda incident you have let us say a scattered light lambda scattered which is Rayleigh scattering or elastic scattering.

But in addition to this there is also inelastic scattering so, lambda inelastic, that is also possible. Now what happens basically here if there is inelastic scattering that means there is exchange of energy between the incident light and the molecule. And that exchange of energy can lead to increase or decrease in energy of the wavelength of this light or increase in decrease in the energy of the light or the wavelength vice versa.

So, I can say that if lambda of scattered light is equal to lambda of incident, then this phenomenon is Rayleigh Scattering. Now if lambda scattered is greater than lambda incident so that means there is increase in the wavelength, then it is called as Stokes Raman Scattering. And similarly, if lambda scattered is less than lambda incident, then it is called as Anti-Stokes Raman scattering. Now why does it happen? Why there is change of energy? Why there is inelastic scattering?

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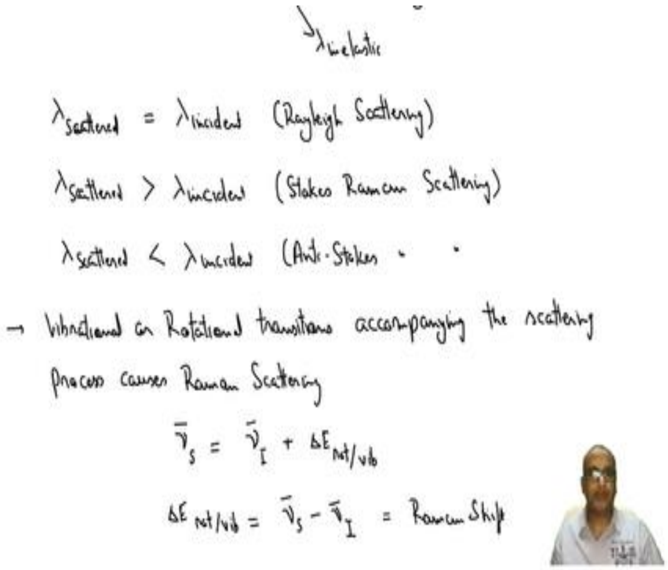

$\lambda_{inelastic}$

$\lambda_{scattered} = \lambda_{incident}$ (Rayleigh Scattering)

$\lambda_{scattered} > \lambda_{incident}$ (Stokes Raman Scattering)

$\lambda_{scattered} < \lambda_{incident}$ (Anti-Stokes " ")

→ Vibrational or Rotational transitions accompanying the scattering process causes Raman Scattering

$$\bar{\nu}_S = \bar{\nu}_I + \Delta E_{rot/vib}$$

$$\Delta E_{rot/vib} = \bar{\nu}_S - \bar{\nu}_I = \text{Raman Shift}$$

So, you can say Vibrational or Rotational transitions accompanying the scattering process causes Raman scattering. So, when you are shining light onto a molecule there is a possibility of scattering and along with scattering there is also a possibility of vibrational or rotational transition. If all of it is happening simultaneously then it causes Raman scattering. So, then we can say that if we talk in terms of nu bar.

So, scattered light the wave number of scattered lights is equal to wave number of incident light plus delta E rotational or vibrational whatever is happening. So, then I can say that delta E rotational slash vibrational can be measured by this change in wave number and this is called as Raman shift.

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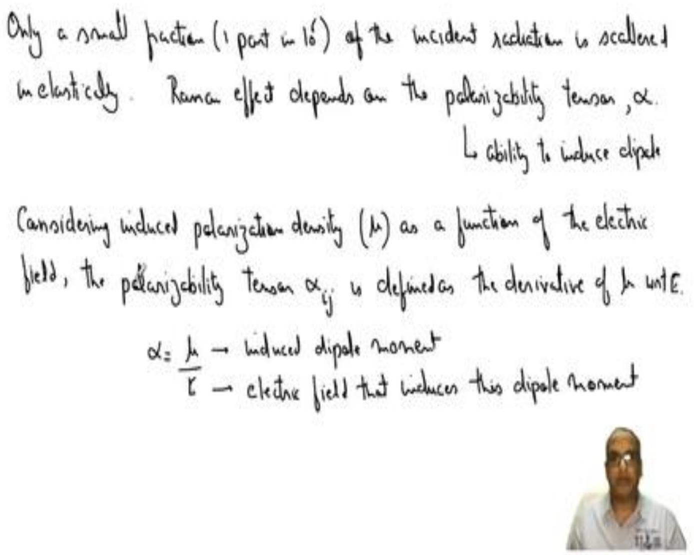

Only a small fraction (1 part in 10^6) of the incident radiation is scattered inelastically. Raman effect depends on the polarizability tensor, α.

↳ ability to induce dipole

Considering induced polarization density (μ) as a function of the electric field, the polarizability tensor α_{ij} is defined as the derivative of μ wrt E.

$\alpha = \frac{\mu}{E}$ → induced dipole moment

→ electric field that induces this dipole moment

Now it is a very small fraction, so only a small fraction that is 1 part in 10 to the power 6 of the incident radiation is scattered inelastically. So, why is that? That is because Raman Effect depends on something called as polarizability tensor which is denoted by the term alpha. So, now what is polarizability tensor? It is basically ability to induce dipoles. So, when you are shining light, it has some electric component which can induce the dipole moment in the molecule.

And that ability is called as polarizability tensor or polarizability which is measured by polarizability tensor. So, just like scalar quantities, vector quantities there are tensor quantities. So, this is a tensor quantity polarizability tensor. So, now let us say if we have, considering induced polarization density which can be written as mu as a function of the electric field. So, I know there is a lot of writing here.

But I think it is important to understand what is different what are different types of spectroscopy. So, that in the later part of this application there is no confusion. The polarizability tensor alpha ij is defined as the derivative of mu with respect to E. Because the change is happening the polarizability is or the polarization is being induced because of E. So, that is how the polarization density divided by E will give you alpha. So, we can say alpha is equal to mu by E which is induced dipole moment and this is the electric field that induces this dipole moment.

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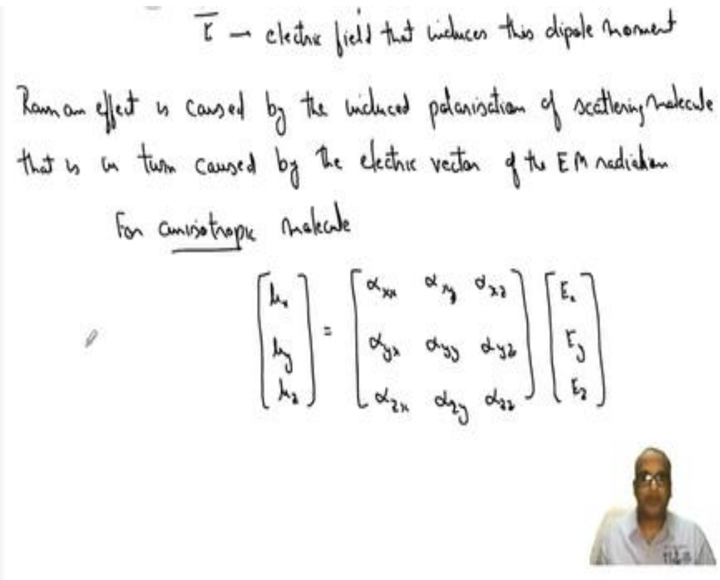

$\bar{E}$ — electric field that induces this dipole moment

Raman effect is caused by the induced polarisation of scattering molecule that is in turn caused by the electric vector of the EM radiation

For anisotropic molecule

$$\begin{bmatrix} \mu_x \\ \mu_y \\ \mu_z \end{bmatrix} = \begin{bmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{bmatrix} \begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix}$$

So, this is easy. So, this is polarizability tensor. Now we can say that the Raman Effect is caused by the induced polarization of molecules that are scattering the light if they are getting polarized. So, they will cause Raman Effect and that is in turn caused by the electric vector of the electromagnetic radiation. So, what we can do is, for anisotropic molecule, go back and read what are an isotropic molecule?

We are not going to discuss what are anisotropic molecules? So, go back and read a little if you do not know. So, mu x mu y and mu z is equal to alpha xx, alpha xy, alpha xz, alpha yx, alpha yy, alpha yz, alpha zx, alpha zy, alpha zz. So, same thing which we had written there now we are writing in terms of matrix. So, you have electric field vector E x, E y, E z.

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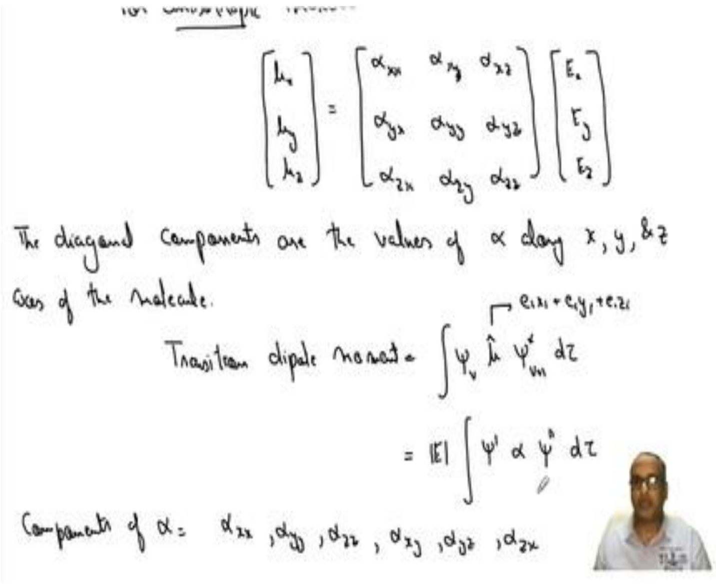

$$\begin{bmatrix}\mu_x\\ \mu_y\\ \mu_z\end{bmatrix} = \begin{bmatrix}\alpha_{xx} & \alpha_{xy} & \alpha_{xz}\\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz}\\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz}\end{bmatrix}\begin{bmatrix}E_x\\ E_y\\ E_z\end{bmatrix}$$

The diagonal components are the values of α along x, y, & z axes of the molecule.

$$\text{Transition dipole moment} = \int \psi_v \overset{e_ix_i + e_iy_i + e_iz_i}{\hat{\mu}} \psi^*_{v+1}\, d\tau$$

$$= |E| \int \psi' \alpha \psi'' \, d\tau$$

Components of $\alpha = \alpha_{xx}, \alpha_{yy}, \alpha_{zz}, \alpha_{xy}, \alpha_{yz}, \alpha_{zx}$

Now the diagonal components are the values of alpha along x, y and z axis of the molecule. And you can see that the longer bond will be easier to polarize than the shorter bond, like if a bond is stronger than it will be difficult to polarize and so on so forth. So, let us also discuss what is we have already seen what is transition dipole moment when we were discussing selection rules. So, transition dipole moment for vibrational spectroscopy is given by psi v mu and psi star we can say v plus 1 d tau.

Now if you remember that mu is here mu is alpha E. But mu forms mu is nothing but e i x i + e i y i + e i z i. If you remember that discussion and this will have x, y and z components and those components can then be treated as the basis for IR representations which transform as x y or z as the basis. So, these will have their own IR representations to which this will form basis. And IR representations for these wave functions can also be determined.

So, you can determine whether this integral will go to 0 or not and accordingly define whether a particular transition will happen or not. Now similarly we can put alpha E here. So, E will come over here and you have same states let us say, this is call it as prime and double prime. So, you have alpha d tau. Now, alpha matrix if you see it has terms as xx, xy, xz, yx. So, these are the binary products of unique vector transformations.

So, these will transform as so the components of alpha will be so we will write down components of alpha, there will be six components because it is a symmetric matrix, alpha xy is equal to alpha yx. so, there will be alpha xx, alpha yy, alpha zz, alpha xy, alpha yz and alpha zx. So, six of these components will be there and all of these will form basis for an IR representation and corresponding IR representations for wave function are also known.

So, you can find out where the Raman Effect will be seen and where it will not be. So, all of this can be group theory rules can be used to identify that. That should be easy to now see.

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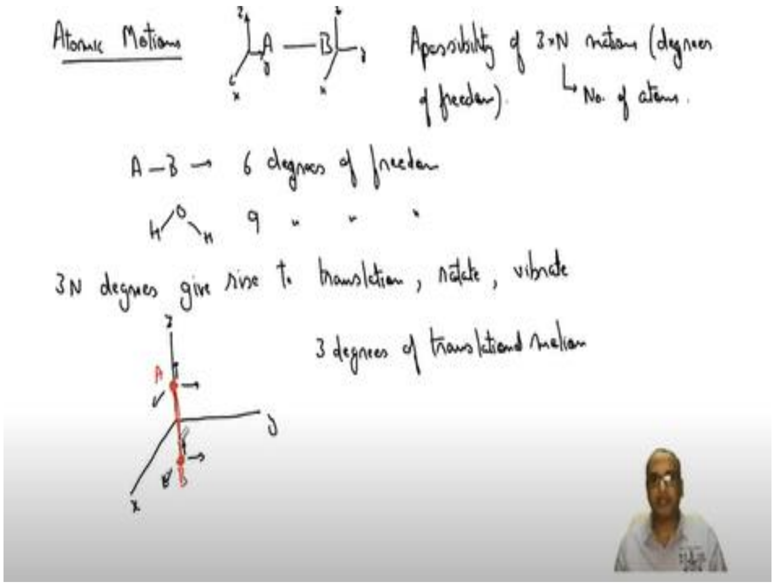

Atomic Motions

A possibility of 3×N motions (degrees of freedom)

No. of atoms.

A–B → 6 degrees of freedom

H–O–H 9 " " "

3N degrees give rise to translation, rotate, vibrate

3 degrees of translational motion

So, next topic that we are going to cover is Atomic Motions. So, what are atomic motion? So, let us consider a diatomic molecule A B. Now this particular atom A, it can move in any direction x, y, z. If this is x, y, z it can move either in x direction y direction z direction, similarly this particular atom can also move in x y and z direction. Now what happens or let us say if it moves in any arbitrary direction then you can always think of those motions as project those motions onto x y and z.

And basically, say that these motions are happening either in x, y or z direction. So, any motion can be projected to x, y and z axis. So, it will have some x, y and z component even if it is an arbitrary motion. So, this gives a possibility of 3 into N motions which are called as degrees of freedom. So, for example a diatomic molecule will have 3 into 2, so N is the number of atoms. So, a diatomic molecule A, B will have 6 degrees of freedom.

Similarly, a triatomic molecule, let us say water, will have 3 into 3, 9 degrees of freedom. So, you can easily calculate how many degrees of freedom or how many possible motions are possible, different type of motions are possible? Now these motions independently these 3N motions 3N degrees or motions give rise to three different types of motions which are translation a molecule can translate in any particular direction that is one motion.

A molecule can rotate or a molecule can vibrate about its mean position. Now let us see how this can happen? So, let us first see that what are the different, let us see how this can happen. Let us see if we have the molecule is like this in x, y, z frame. So, you have let me draw the molecule with a different colour. So, I have A and B, this is my molecule. Now let us say if these two atoms if both of them move in x-axis along x-axis;

That is possible, that is one way of moving out of six one way of moving is this, second way of moving is this along y axis third way of moving is both atoms will move simultaneously in one direction which will give you three degrees of translational motion. Now any given molecule it is possible for any given molecule I am just taking example of a diatomic molecule.

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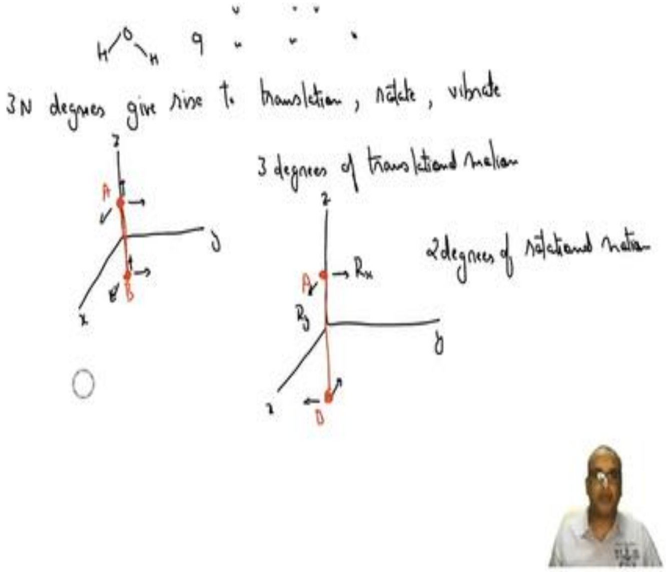

But any given molecule should be able to do this type of motion where all the atoms are either moving in x direction, y direction, or z direction. Or if it is moving in any random direction you can still get the projections onto x axis y axis and z axis. So, there must be every molecule must possess three translational degrees of freedom, or three degrees of translational motion either way you can explain.

Now let us see what are the other possibilities? So, let us draw this molecule again in the same frame x, y, z, A and B. Now let us say if I say that A moves in this direction and B moves in this direction. Now they are not moving in same direction which was causing the translation. If A moves in this direction and B moves in this direction, effectively, they are rotating about x axis. So, this is one rotational degree of freedom.

Similarly, if A moves in positive x axis and B moves in negative x axis this will move in with respect to y axis. So, this is rotation about x axis this motion is rotation about y axis. And third is like if they move about z axis how would you define? There would be third motion which can be defined by moving about z axis which will not happen in this case or which will happen but it will not cause any change in the molecule.

For quantum molecules you will not be able to quantum objects you will not be able to identify whether a change is happening or not if it is moving about its own axis. So, there would be two degrees of rotational motion. Let us also take an example of a non-linear molecule.

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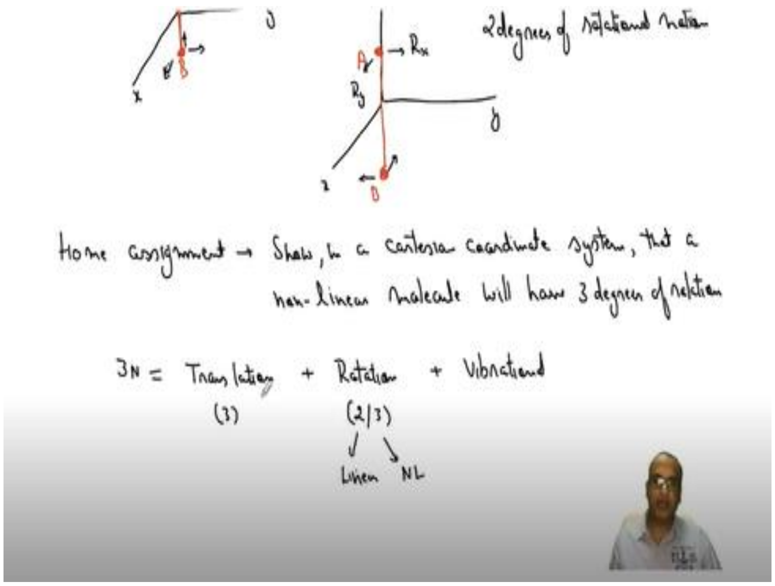

Home assignment → Show, in a cartesian coordinate system, that a non-linear molecule will have 3 degrees of rotation

$$3N = \underset{(3)}{\text{Translation}} + \underset{(2/3)}{\text{Rotation}} + \text{Vibrational}$$

So, that we know that for nonlinear molecule there should be three such degrees. Let us try to see if we can or let us take it as a home assignment rather. So, home assignment again it will depend upon how you can visualize. So, show in a cartesian coordinate system that a non-linear molecule will have 3 degrees of rotation. So, that you should be able to draw and sketch it out. So, if there are 3 translational 2 rotational so what is left now?

So, out of three N we have translation possible, we have seen that 3 will be contributing to translation plus rotation possible. So, rotation it will be either 2 or 3 depending on whether it is a linear or non-linear molecule. This is for linear and this is for non-linear. So, the rest of the degrees will be vibrational degrees. So, for example if A moves here and B moves here it will cause vibration of the bond.

If A moves downwards B moves upwards then also it will cause vibration of the molecule. So, rest of the degrees are vibrational degrees of freedom.

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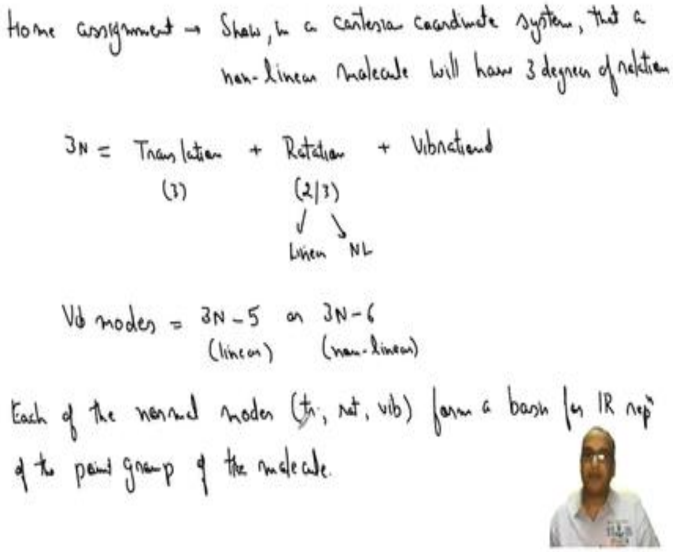

Home assignment → Show, in a cartesian coordinate system, that a non-linear molecule will have 3 degrees of rotation

3N = Translation + Rotation + Vibrational
(3) (2/3)
Linear NL

Vib modes = 3N − 5 or 3N − 6
(linear) (non-linear)

Each of the normal modes (tr, rot, vib) form a basis for IR repn of the point group of the molecule.

So, we can say here that vibrational modes, is equal to 3N - 5 or 3N – 6, this is for linear molecules and this is for non-linear molecules. So, this is easy to see. Now you can also appreciate the fact that each of the normal modes can be translational rotational or vibrational or we can write down here translational, rotational, vibrational forms a basis for IR representation of the point group.

See everything in this course you go and then finally it will form a basis for IR representation of the point group. So, that is how the beauty of this subject is that you can actually correlate everything to the symmetry of that particular molecule and then talk about the physical properties. So, here each of the normal modes forms a basis for IR representation of the point group of the molecule.

We will see how to use this in next class by doing local coordinate analysis. And we will see how to actually find out the different vibrations? How to visualize different vibrational modes? That is all for today.